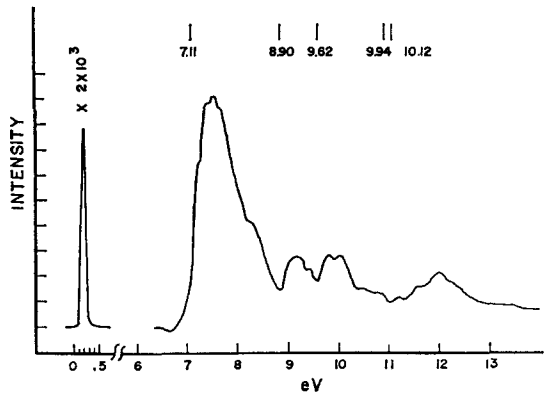


FIG. 2. Electron-impact spectrum of ethylene. Incident electron energy: 50 eV, scattering angle: $\theta<20$ mrad. The positions of the Rydberg band heads are shown above. The resolution may be judged by the width of the primary peak.

impact spectra as the scattering angle approaches zero should show the same features as the ultraviolet absorption.

Since the measurements of Kuppermann and Raff were made apparently at high scattering angle and energies below that at which the Born approximation would be expected to apply, it is of interest to determine whether the deviations are a result of the large angle scattering or the low energy.

Our measurements were made with a nearly monoenergetic electron beam of energy half-width $<0.1$ eV analyzed in the forward direction ($\theta<20$ mrad). Both the filtering analyzer (monochromator) and the post analyzer were of the deflection type in which no differentiation was required. The energy sweep was obtained by determining the amount of energy that must be added to return those electrons that have lost energy to the primary value. With this method of measurement the measured energy losses are independent of contact potentials and no corrections need be applied. The energy loss is read directly from the instrument.

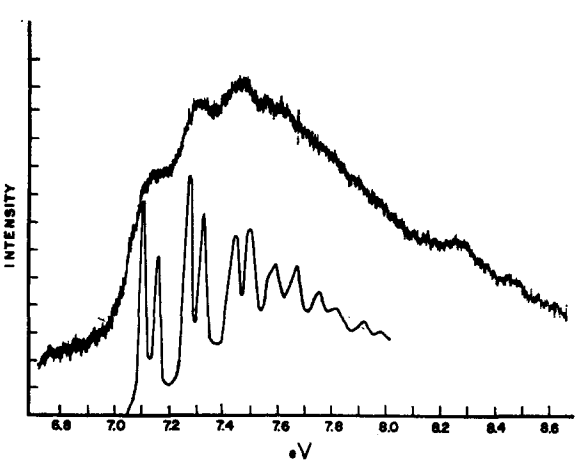


FIG. 3. High-resolution electron-impact spectrum of the first band of ethylene. Untouched recording trace shown below is ultraviolet absorption spectra of Zelikoff and Watanabe. The resolution is superior in the uv measurements in this wavelength region but the advantage is less significant below 1000 Å.

Figure 1 shows the zero-angle inelastic electron spectrum for He. Note that neither the $2^3S$ state nor the ionization limit are prominent. Figures 2 and 3 show the electron impact spectrum of ethylene. The position of the band heads of the Rydberg series as determined by Price and Tutte[4] are shown in Fig. 2. Figure 3 shows the excellent agreement with the ultraviolet measurements of Zelikoff and Watanabe[5] on the fine structure of the first band.

The data force the conclusion, therefore, that deviations from optical spectra observed by Kuppermann and Raff are a consequence of the high angular scattering, rather than any marked deviation from the Born approximation at 50-eV primary energy.

[1] A. Kuppermann and L. M. Raff, J. Chem. Phys. **34**, 2497 (1962).
[2] H. A. Bethe, Ann. Physik **5**, 325 (1930).
[3] E. N. Lassettre, Radiation Res. Suppl. **1**, 530 (1959).
[4] W. C. Price and W. T. Tutte, Proc. Roy. Soc. (London) **A174**, 207 (1940).
[5] M. Zelikoff and K. Watanabe, J. Opt. Soc. Am. **43**, 756 (1953).

## Differences between Low-Energy Electron-Impact Spectra at 0° and at Large Scattering Angle*

ARON KUPPERMANN AND LIONEL M. RAFF†
*Department of Chemistry, University of Illinois, Urbana, Illinois*
(Received 3 June 1963)

THE preceding Comment reports some low-energy electron-impact spectra of helium and ethylene, obtained by a very elegant technique, which are markedly different from the ones we obtained[1] under other experimental conditions. It is quite important to try to understand the reasons for the differences observed. These differences are essentially the following: (a) In our impact spectra of helium obtained with 50-eV electrons we observe pronounced peaks corresponding to the $2\ ^3S$ state and to ionization whereas Simpson and Mielczarek do not. (b) In our spectra of ethylene at this same incident electron energy we observe two pronounced optically forbidden transitions and a well-defined ionization peak whereas they do not.

In our experiments, described in detail elsewhere,[1b] only electrons with a scattering angle between 22° and 112° can be detected, the 90° ones being most favored. Thus, it is interesting to analyze the differences between the two sets of results mentioned above in the light of the angular dependence of scattering cross sections.

Let us consider initially the transition to the $2\ ^3S$ state in helium. From Simpson and Mielczarek's Fig. 1 we conclude that its cross section at 0° is at least two

orders of magnitude smaller than that for the transition to the $2\,^1P$ state, whereas from Fig. 1 of Ref. 1(a) those two cross sections are of the same order of magnitude at large angles. The question arises as to whether the ratio of the cross sections of the transitions under consideration can indeed be such a steep function of the scattering angle. Ideally, such a question should be answered experimentally by obtaining angular scattering curves in the same instrument. Within the framework of the Born–Oppenheimer scattering approximation,[2] the angular distribution of the scattered electrons for optically allowed transitions falls very steeply as the angle of scattering increases, whereas for spin-forbidden transitions this distribution is very much more nearly uniform.[3] Therefore, the Born–Oppenheimer approximation and the two sets of observations are not necessarily inconsistent with each other.

Within the framework of the Born approximation, up to angles for which the magnitude $\Delta P$ of the change in the momentum vector of the electron is sufficiently small,[4] optically forbidden (but spin-allowed) transitions, such as the $1\,^1S \rightarrow 2\,^1S$ one in helium and, presumably, the 6.5-eV one in ethylene, have a cross section which is approximately independent of angle, whereas for optically allowed transitions it is inversely proportional to the square of that momentum change. Therefore the ratio of the cross sections of an optically forbidden (but spin-allowed) and an optically allowed transition increases with scattering angle, consistent with the two sets of observations. However, at scattering angles of 90°, $\Delta P$ becomes large and the power series expansion on which this conclusion is based[5] is no longer valid.

We were somewhat surprised at finding well-formed ionization peaks, but they are systematically present in all experiments we have performed. They might be a characteristic of large scattering angles.

It is very important to remember that the validity of the Born approximation depends not only on the energy of the incident electron, but also on the scattering angle. Thus, at a given incident energy, the Born approximation could still be valid at small scattering angles but not at large ones.[6] The differences between the two sets of results is therefore consistent with the assumption that at 50-eV incident energy, for helium, the Born approximation is good at 0° scattering but bad at 90°. It should be stressed, however, that the fact that Simpson and Mielczarek's spectra at 0° show the same features as the ultraviolet absorption spectra is a necessary but far from sufficient condition for the validity of the Born approximation. A sufficient test would require the measurement of the dependence of the cross sections on $\Delta P$, as done by Lassettre[4] in the 500-eV energy range. Consequently, the only conclusion which should be derived from those results is that for incident electrons of 50 eV scattered at 0° by helium or ethylene the Born approximation is not necessarily wrong. The conclusion that may be derived from our results is that under similar conditions, but at large scattering angles, the minimum correction to the Born approximation needed (since it rigorously excludes the $2\,^3S$ transition) is the inclusion of exchange scattering through the Born–Oppenheimer approximation, and that the latter is not necessarily wrong at those angles. It should be stressed, however, that there is independent evidence of the poorness of the Born–Oppenheimer approximation at such low energies. For example, Massey and Moiseiwitsch[7] have shown that such approximation clearly overestimates the total cross section for the $1\,^1S \rightarrow 2\,^3S$ transition by a factor of at least 20 in the incident-energy range of 21 to 50 eV.

In summary, we reach the following conclusions:

(a) The differences between Simpson and Mielczarek's spectra and our own are due to the differences in scattering angles and are not inconsistent with each other.

(b) Since we observe, very clearly, the $1\,^1S \rightarrow 2\,^3S$ transition in helium for 50-eV electrons and large scattering angles, the Born approximation is necessarily wrong under those conditions. The fact that this transition was not observed at 0° scattering angle does not contradict this conclusion.

(c) None of the electron-impact spectra mentioned contradict Massey and Moiseiwitsch's conclusion about the poorness of the Born–Oppenheimer (plane-wave) approximation at 50-eV incident energy.

* This work was supported in part by the U. S. Atomic Energy Commission.

† Present address: Department of Chemistry, Columbia University, New York 27, New York.

[1] A. Kuppermann and L. M. Raff, (a) J. Chem. Phys. **37**, 2497 (1962). In Fig. 1 of this reference the ionization potential of ethylene, which should be 10.5 eV, appears as 10.0 eV due to a typographic error; (b) Discussions Faraday Soc. (to be published).
[2] J. R. Oppenheimer, Phys. Rev. **32**, 361 (1928).
[3] H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Oxford University Press, London, 1952), p. 157.
[4] E. N. Lassettre, Radiation Res., Suppl. **1**, 530 (1959).
[5] Reference 4, Eq. (4).
[6] Reference 3, p. 127.
[7] H. S. W. Massey and B. L. Moiseiwitsch, Proc. Roy. Soc. (London) **A227**, 38 (1954).

## Erratum and Further Comments: Vibrational Excitons. II. Degenerate Vibrations

[J. Chem. Phys. **36**, 2285 (1962)]

R. M. HEXTER
*Mellon Institute, Pittsburgh, Pennsylvania*

(Received 26 April 1963)

SEVERAL errors in Sec. IV (Cubic Crystals) of this paper have been pointed out by D. Fox of the State University of New York. Although corrections of